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(54) COATED STEEL SHEET EXCELLENT IN CORROSION RESISTANCE

(57)Abstract:

PROBLEM TO BE SOLVED: To produce a coated steel sheet which is subjected to rust preventive treatment with a chrome-free substrate treating agent to take place of chromic acid treatment and phosphate treatment and has excellent corrosion resistance.

SOLUTION: This coated steel sheet having the excellent corrosion resistance is obtained by forming a film consisting of the substrate treating agent containing (A) an aqueous liquid containing at least one kind of a titanium compound selected from a hydrolyzable titanium compound, a low condensate of the hydrolyzable titanium compound, titanium hydroxide and a low condensate of the titanium hydroxide (B) at least one kind of a compound selected from a phosphoric acid-base compound, metal hydrofluoric acid and a metallic hydrofluorate and (C) an aqueous organic high-molecular compound stable at a pH ≤ 7 on the surface of a substrate metallic material and forming a finish coating film through or without through a primer coating film on the surface treated film.

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CLAIMS

[Claim(s)]

[Claim 1] On the front face of a substrate metallic material, (A) hydrolysis nature titanium compound, a hydrolysis nature titanium compound low condensate. The aqosity liquid containing the titanium which at least one sort of titanium compounds and hydrogen peroxide solution which are chosen from hydroxylation titanium and a hydroxylation titanium low condensate are made to react, and is obtained. (B) At least one sort of compounds chosen from a phosphoric-acid system compound, metal hydrofluoric acid, and a metal hydrofluoric acid salt. And the paint steel plate excellent in the corrosion resistance in which the coat by the surface treatment agent characterized by containing a stable aqosity organic high molecular compound by seven or less (C) PH is formed in, and it comes to form a finishing paint film, without minding through an under coat paint film on this surface treatment coat.

[Claim 2] The paint steel plate according to claim 1 characterized by being the aqosity liquid (A-1) with which aqosity liquid (A) contains the titanium which a hydrolysis nature titanium compound and/or a hydrolysis nature titanium compound low condensate, and hydrogen peroxide solution are made to react, and is obtained under existence of a titanium oxide sol.

[Claim 3] The paint steel plate according to claim 1 or 2 characterized by for aqosity liquid (A) adding a titanium compound and manufacturing it in hydrogen peroxide solution.

[Claim 4] A paint steel plate given in claim 1 characterized by being a titanium monomer containing the radical from which a hydrolysis nature titanium compound hydrolyzes and

becomes a hydroxyl group thru/or any 1 term of 3.

[Claim 5] A paint steel plate given in claim 1 characterized by being the low condensate of the titanium monomer containing the radical from which a hydrolysis nature titanium compound low condensate hydrolyzes, and becomes a hydroxyl group thru/or any 1 term of 3.

[Claim 6] A paint steel plate given in claim 1 to which a hydrolysis nature titanium compound is characterized by being a general formula (OR) Ti 4 (the inside of a formula and R being the same -- or it differing and the alkyl group of carbon numbers 1-5 being shown) thru/or any 1 term of 4.

[Claim 7] The paint steel plate according to claim 1, 2, or 5 with which the above-mentioned low condensate is characterized by being 2-30 whenever [condensation].

[Claim 8] A paint steel plate given in claim 1 to which the mixed rate of a titanium compound and hydrogen peroxide solution is characterized by a hydrogen peroxide being the 0.1 - 100 weight section to the titanium compound 10 weight section thru/or any 1 term of 3.

[Claim 9] The paint steel plate according to claim 1 characterized by compounds (B) being at least one sort of compounds chosen from a phosphoric acid, a metaphosphoric acid, a condensed phosphoric acid, a condensation metaphosphoric acid, phosphate, a metaphosphate, a condensed phosphate, a condensation metaphosphate, zirconium hydrofluoric acid, titanium hydrofluoric acid, silicofluoric acid, a zirconium fluoridation salt, a titanium fluoridation salt, and *****.

[Claim 10] The paint steel plate according to claim 1 or 9 with which the blending ratio of coal of a compound (B) is characterized by being the 1 - 400 weight section to the solid content 100 weight section of the aqosity liquid (A) containing titanium.

[Claim 11] The paint steel plate according to claim 1 characterized by an aqosity organic high

molecular compound (C) being an aqosity organic high molecular compound chosen from at least one sort of resin of epoxy system resin, phenol system resin, acrylic resin, urethane system resin, polyvinyl alcohol system resin, polyalkylene glycol system resin, and olefin-carboxylic-acid system resin.

[Claim 12] The paint steel plate according to claim 1 or 11 with which the blending ratio of coal of an aqosity organic high molecular compound (C) is characterized by being the 10 - 2,000 weight section to the solid content 100 weight section of the aqosity liquid (A) containing titanium.

[Claim 13] A paint steel plate given in claim 1 to which a surface treatment agent is characterized by being the aqosity liquid of PHs 1-7 thru/or any 1 term of 12.

[Claim 14] On the front face of a substrate metallic material, (A) hydrolysis nature titanium compound, a hydrolysis nature titanium compound low condensate. The aqosity liquid containing

the titanium which at least one sort of titanium compounds and hydrogen peroxide solution which are chosen from hydroxylation titanium and a hydroxylation titanium low condensate are made to react, and is obtained. (B) At least one sort of compounds chosen from a phosphoric-acid system compound, metal hydrofluoric acid, and a metal hydrofluoric acid salt. And the surface treatment agent characterized by containing a stable aqosity organic high molecular compound by seven or less (C) PH is applied so that desiccation thickness may be set to 0.001-10 micrometers. The manufacture approach of a paint steel plate excellent in the corrosion resistance in which a finishing paint film is made to form without minding through an under coat paint film on this surface treatment coat after making it dry.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] It is related with the paint steel plate excellent in corrosion resistance which performed chromate treatment and rustproofing by the surface treatment agent of the chromium free-lancer who replaces phosphate processing.

[0002]

[Description of the Prior Art] Conventionally, as surface treatment to metal bases, such as cold rolled sheet steel, a zinc system plating steel plate, and an aluminum steel plate, although chromate treatment and phosphoric-acid zinc processing are generally performed, the toxicity of chromium has been a problem. Chromate treatment has requiring great costs, a problem by the elution of the chromic acid from a chemical conversion coat, etc. in the problem of the vaporization of the chromate fume in down stream processing, and a waste-water-treatment facility further. Moreover, many public engines specify chromate compounds as the carcinogen to the body by making IARC (International Agency for Researchon Cancer Review) into the start, and they are very harmful matter.

[0003] Moreover, in phosphoric-acid zinc processing, in order to perform rinse processing by the chromic acid, while there is usually a problem of chroming after phosphoric-acid zinc processing, there is a problem of waste water treatment, such as a reaction accelerator in a phosphoric-acid zinc processing agent and a metal ion, and the sludge treatment by the elution of the metal ion from a processed metal.

[0004] After processing in the water solution containing (1) pile aluminum phosphate as arts other than chromate treatment or phosphoric-acid zinc processing, the art which the approach (refer to JP.51-71233A) of processing in the water solution containing the surface treatment approach (referring to JP.53-28857B) heated at the temperature of 550 degrees C and 150 - (2) tannic acid etc. was proposed, and combined the art or these by (3) sodium nitrites, sodium borate, the imidazole, aromatic carboxylic acid, a surfactant, etc. is performed.

[0005] However, the approach of (1) does not have the enough adhesion of a coating, when painting a coating on this, and the approach of (2) is inferior in corrosion resistance, and each of approaches of (3) has the problem that the corrosion resistance at the time of being exposed to the ambient atmosphere of heat and high humidity is inferior.

[0006] Moreover, as a zinc system steel plate which has the coat of the thin film of thickness several micrometers or less, the rust-proofing steel plate which used the zinc system plating steel plate as the base material, formed the clo mate coat in this, and formed the organic compound silicate coat as the maximum upper layer on this further is known by JP.58-224174A, JP.60-50179A, and JP.60-50180A, and this thing has the engine performance excellent in workability and corrosion resistance in them. However, since this rust-proofing steel plate had a clo mate coat, it had the problem of the insurance health side by clo mate ion similarly with having described above. Moreover, the steel plate except this rust-proofing steel plate to a clo mate coat is not yet enough as corrosion resistance.

[0007] Moreover, the phosphoric-acid compound which did not participate in coat formation needs to precipitate as a sludge, and phosphate processing needs to process this sludge as

industrial waste, and has problems, such as an environmental cure and abandonment processing cost.

[0008] The purpose of this invention is offering the paint steel plate excellent in corrosion resistance which performed chromate treatment and rustproofing by the surface treatment agent of the chromium free-lancer who replaces phosphate processing.

[0009]

[Means for Solving the Problem] this invention persons came to complete a header and this invention for the paint steel plate which comes to use the surface treatment agent which comes to blend at least one sort of compounds chosen from the aqosity liquid which contains specific titanium as a rust-proofer for metals, a phosphoric-acid system compound, metal hydrofluoric acid, and a metal hydrofluoric acid salt, and an aqosity organic high molecular compound being what attains the above-mentioned purpose.

[0010] According to this invention in this way On the front face of a substrate metallic material, (A) hydrolysis nature titanium compound, The aqosity liquid containing the titanium which at least one sort of titanium compounds and hydrogen peroxide solution which are chosen from a hydrolysis nature titanium compound low condensate, hydroxylation titanium, and a hydroxylation titanium low condensate are made to react, and is obtained, (B) At least one sort of compounds chosen from a phosphoric-acid system compound, metal hydrofluoric acid, and a metal hydrofluoric acid salt, And the paint steel plate excellent in the corrosion resistance in which the coat by the surface treatment agent characterized by containing a stable aqosity organic high molecular compound by seven or less (C) PH is formed in, and a finishing paint film is formed, without minding through an under coat paint film on this surface treatment coat is offered.

[0011]

[Embodiment of the Invention] The paint steel plate of this invention has the description in the front face of a substrate metallic material at the place which forms the surface treatment coat by the specific surface treatment agent instead of chromate treatment or phosphate processing, and can obtain the paint steel plate excellent in corrosion resistance by forming a finishing paint film, without minding through an under coat paint film on this surface treatment coat.

[0012] First, the above-mentioned surface treatment agent is explained.

[0013] The surface treatment agent used for surface treatment agent this invention contains at least one sort of compounds (B) and the aqosity organic high molecular compound (C) which are chosen from the aqosity liquid (A) containing titanium, a phosphoric-acid system compound, metal hydrofluoric acid, and a metal hydrofluoric acid salt.

[0014] The aqosity liquid (A) containing the titanium used by the aqosity (liquid A) surface treatment agent containing titanium is the aqosity liquid containing the titanium which at least one sort of titanium compounds and hydrogen peroxide solution which are chosen from a hydrolysis nature titanium compound, a hydrolysis nature titanium compound low condensate, hydroxylation titanium, and a hydroxylation titanium low condensate are made to react, and is obtained. As this aqosity liquid, if it describes above, a well-known thing can be especially used without a limit from the former, choosing it suitably.

[0015] The above-mentioned hydrolysis nature titanium compound is a titanium compound which has the hydrolysis nature machine coupled directly with titanium, and generates hydroxylation titanium by reacting with the moisture of water, a steam, etc. Moreover, in a hydrolysis nature titanium compound, whether all the radicals combined with titanium are hydrolysis nature machines or it is the hydroxyl group with which the one section was hydrolyzed, neither is available.

[0016] Although it will not be restricted especially if hydroxylation titanium is generated by [above-mentioned] reacting with moisture like as a hydrolysis nature machine, the radicals (for example, halogen atoms (chlorine etc.), a hydrogen atom, sulfate ion, etc.) which form a low-grade alkoxyl group, titanium, and a salt are mentioned, for example.

[0017] especially as a hydrolysis nature titanium compound which contains a low-grade alkoxyl group as a hydrolysis nature machine, the tetra-alkoxy titanium of a general formula (OR) Ti 4 (the inside of a formula and R are the same -- or it differs and the alkyl group of carbon numbers 1-5 is shown) is desirable. As an alkyl group of carbon numbers 1-5, a methyl group, an

ethyl group, n-propyl group, an iso-propyl group, n-butyl, iso-butyl, sec-butyl, tert-butyl, etc. are mentioned, for example.

[0018] Moreover, as a hydrolysis nature titanium compound which has the radical which forms titanium and a salt as a hydrolysis nature machine, a titanium chloride, sulfuric-acid titanium, etc. are mentioned as a typical thing.

[0019] A hydrolysis nature titanium compound low condensate is the above-mentioned low condensate of hydrolysis nature titanium compounds. Whether all the radicals combined with the one section was hydrolyzed, neither is available for it.

[0020] Moreover, the altitanic acid (hydroxylation titanium gel) obtained by the reaction of water solutions, such as a titanium chloride and sulfuric-acid titanium, and alkali solutions, such as ammonia and caustic alkali of sodium, can also be used as a low condensate.

[0021] The compound of 2-30 is usable, and as aqosity liquid (A) with desirable using the thing of 2-10 within the limits especially whenever [condensation], whenever [in the above-mentioned hydrolysis nature titanium compound low condensate or the above-mentioned

hydroxylation titanium low condensate / condensation] can use a well-known thing without a limit especially from the former, if it is the aqosity liquid containing the titanium obtained by making the above-mentioned titanium compound and hydrogen peroxide solution react.

Specifically, the following can be mentioned.

[0022] ** The titanion hydrogen-peroxide complex or titanic-acid (pel oxo-titanium hydrate) water solution (refer to JP.63-35419.A and JP.1-224220.A) which adds hydrogen peroxide solution to the gel or the sol of water titanium oxide, and is obtained.

[0023] ** The liquid for titania film formation obtained by making hydrogen peroxide solution act on the hydroxylation titanium gel manufactured from the titanium chloride, the sulfuric-acid titanium water solution, and the basic solution, and compounding (refer to JP.9-71418.A and JP.10-67516.A).

[0024] Moreover, in the above-mentioned liquid for titania film formation, the hydroxylation titanium gel called an altitanic acid is settled by making titanium, the titanium chloride which has the radical which forms a salt and a sulfuric-acid titanium water solution, and alkali solutions, such as ammonia and caustic alkali of sodium, react. Subsequently, a yellow transparent viscous liquid can be obtained by separating hydroxylation titanium gel, rinsing well, adding hydrogen peroxide solution further, and carrying out decomposition removal of the excessive hydrogen peroxide by the decantation using water.

[0025] This altitanic acid that described above and precipitated is in the gel state giant-molecule-sized by OH comrade's polymerization and hydrogen bond, and cannot be used as aqosity liquid which contains titanium the way things stand. If hydrogen peroxide solution is added to this gel, a part of OH will be in a peroxidation condition, the dissolution or a macromolecule chain will be in a kind of sol condition divided by low-molecular as peroxotitanic acid ion, it becomes water and oxygen, and decomposes and an excessive hydrogen peroxide can be used now as aqosity liquid containing the titanium for inorganic film formation.

[0026] Since this sol contains only an oxygen atom and a hydrogen atom in addition to a titanium atom and it generates only water and oxygen when changing with desiccation or baking to titanium oxide, it does not need removal of a carbon component required for pyrolyses, such as a sol gel process, and a sulfate, or a halogen component, but can create the crystalline titanium oxide film with a comparatively high consistency also at low temperature conventionally.

[0027] ** Add a hydrogen peroxide to the inorganic titanium compound water solution of a titanium chloride or sulfuric-acid titanium, and make a ** RUOKISO titanium hydrate form. After making the precipitate of a pel oxo-titanium hydrate polymer form by leaving or heating the solution which added the alkali to this and was obtained. The solution for titanic-acid ghost formation which remove dissolution components other than the water which originates in a titanium content raw material solution at least, and a hydrogen peroxide is made to act further, and is obtained (refer to JP.2000-247638.A and JP.2000-247639.A).

[0028] the aqosity liquid (A) used by this invention --- the above --- although the aqosity liquid containing the titanium obtained by the well-known approach can be used, the aqosity liquid

containing the titanium further obtained by the approach of adding and manufacturing a titanium compound in hydrogen peroxide solution can be used. it is desirable to use the hydrolysis nature titanium compound which contains the radical which is expressed with said general formula (OR) Ti 4 (the inside of a formula and R are the same --- or it differs and the alkyl group of carbon numbers 1-5 is shown), and which hydrolyzes and turns into a hydroxyl group as this titanium compound, and its hydrolysis nature titanium compound low condensate.

[0029] The mixed rate of a hydrolysis nature titanium compound and/or its low condensate (these things are only hereafter abbreviated to "hydrolysis nature titanium compound a"), and hydrogen peroxide solution has desirable within the limits of the 0.1 - 100 weight section, especially 1 - 20 weight section to the hydrolysis nature titanium compound a 10 weight section at hydrogen-peroxide conversion. If it becomes under the 0.1 weight section by hydrogen-peroxide conversion, chelate formation will not be enough and will carry out nebula precipitate. On the other hand, since active oxygen dangerous during storage will be emitted that an unreacted hydrogen peroxide tends to remain if the 100 weight sections are exceeded, it is not desirable.

[0030] Although especially the hydrogen-peroxide concentration of hydrogen peroxide solution is not limited, it is desirable that it is 3 - 30% of the weight of within the limits in respect of the solid content of generation liquid related to paint workability in the ease of dealing with it.

[0031] Moreover, the aqosity liquid (A) which comes to use hydrolysis nature titanium compound a can be manufactured by making hydrolysis nature titanium compound a react for 10 minutes to 20 hours by within the limits with a hydrogen peroxide solution and a reaction temperature of 1-70 degrees C.

[0032] The aqosity liquid (A) which comes to use hydrolysis nature titanium compound a By making hydrolysis nature titanium compound a and hydrogen peroxide solution react Hydrolyze with water and a hydrolysis nature titanium compound generates a hydroxyl-group content titanium compound. Subsequently, it is imagined as what is configured in the hydroxyl-group content titanium compound which the hydrogen peroxide generated, when the coordination by this hydrolysis reaction and hydrogen peroxide happens near the coincidence, it is obtained, and the chelate liquid with which stability is equal to long-term, very high preservation in a room temperature region is generated. Hydroxylation titanium gel used by the conventional process is partially three-dimensions-sized by Ti-O-Ti association, and this gel essentially differs from the object to which hydrogen peroxide solution was made to react about a presentation and stability.

[0033] The titanium oxide dispersion liquid containing the ultrafine particle of the titanium oxide which crystalized the aqosity liquid (A) which comes to use hydrolysis nature titanium compound a when heat-treatment or autoclave processing was performed above 80 degrees C are obtained. At less than 80 degrees C, crystallization of titanium oxide does not fully progress. Thus, the range of 10nm or less of particle diameter of a titanium oxide ultrafine particle of the manufactured titanium oxide dispersion liquid is 1nm - 6nm preferably. Moreover, the appearance of these dispersion liquid is a translucent-like thing. Since film formation nature will fall if this particle diameter becomes larger than 10nm (a crack is produced in 1 micrometers or more), it is not desirable. These dispersion liquid can be used similarly.

[0034] The aqosity liquid (A) which comes to use hydrolysis nature titanium compound a can form the precise titanium oxide film which was excellent in adhesion with itself by heat-treating at spreading desiccation or low temperature into a steel plate ingredient.

[0035] Especially as heat-treatment temperature, it is desirable to form 200 degrees C or less of titanium oxide film at the temperature of 150 degrees C or less, for example.

[0036] The aqosity liquid (A) which comes to use hydrolysis nature titanium compound a forms the titanium oxide film of the amorphous substance (amorphous) which contains a hydroxyl group a little with the above-mentioned temperature.

[0037] Moreover, since the titanium oxide dispersion liquid which carried out heat-treatment of 80 degrees C or more can form the crystalline titanium oxide film only by applying, they are useful as a coating material of the ingredient whose heat-treatment is impossible.

[0038] In this invention, the aqosity liquid (it abbreviates to "aqosity liquid (A-1)" hereafter)

containing the titanium which the same hydrolysis nature titanium compound as the above and/or a hydrolysis nature titanium compound low condensate, and hydrogen peroxide solution are made to react, and is further obtained under existence of a titanium oxide sol as aqosity liquid (A) can be used, it is desirable to use the titanium monomer containing the radical which is expressed with the above-mentioned general formula (OR) Ti 4 (the inside of a formula and R are the same -- or it differs and the alkyl group of carbon numbers 1-5 is shown) as a hydrolysis nature titanium compound and/or a hydrolysis nature titanium compound low condensate (hydrolysis nature titanium compound a) and which hydrolyzes and turns into a hydroxyl group, and its hydrolysis nature titanium compound low condensate.

[0039] The above-mentioned titanium oxide sols are a non-fixed form titania and a sol which the anatase titania particle distributed in water (aqosity organic solvents, such as an alcoholic system and an alcoholic ether system, may be contained if needed).

[0040] As the above-mentioned titanium oxide sol, a well-known thing can be used from the former. What hydrolyzes ** titanium solutions, such as (1) sulfuric-acid titanium and sulfuric-acid titanil, for example, and is obtained as this titanium oxide sol, (2) What hydrolyzes organic titanium compounds, such as a titanium alkoxide, and is obtained, (3) What calcinated the non-fixed form titania sol and this titanium oxide aggregate which distributed in water titanium oxide aggregates, such as what hydrolyzes or neutralizes and can obtain halogenation titanium solutions, such as a titanium tetrachloride, considered as the anatase titanium particle, and distributed this thing in water can be used. Baking of an amorphous titania can transform an amorphous titania to an anatase mold titania, if it calcinates at the temperature beyond the crystallization temperature of anatase, for example, the temperature of 400 degrees C - 500 degrees C or more, at least. As hydrosol of this titanium oxide, TKS-201 (the TAYCA [CORP.] CORP. make, a trade name, anatase crystal form, mean particle diameter of 6nm), TA-15 (the Nissan Chemistry company make, a trade name, anatase crystal form), STS-11 (the Ishihara Sangyo [Kaisha, Ltd.] Kaisha, Ltd. make, a trade name, anatase crystal form), etc. are mentioned.

[0041] the weight ratio of the above-mentioned titanium oxide sol at the time of using it in order to make hydrolysis nature titanium compound a and hydrogen peroxide solution react, and a titanium hydrogen-peroxide reactant -- 1/99 - 99/1 -- it is 90/[about 10/90 -] 10 range preferably. Since film formation nature is inferior when the effectiveness which added titanium oxide sols, such as stability and photoreaction nature, will not be seen if a weight ratio becomes less than 1/99, but 99/1 is exceeded, it is not desirable.

[0042] The mixed rate of hydrolysis nature titanium compound a and hydrogen peroxide solution has desirable within the limits of the 0.1 - 100 weight section, especially 1 - 20 weight section to the hydrolysis nature titanium compound a 10 weight section at hydrogen-peroxide conversion. If it becomes under the 0.1 weight section by hydrogen-peroxide conversion, chelate formation will not be enough and will carry out nebula precipitate. On the other hand, since active oxygen dangerous during storage will be emitted that an unreacted hydrogen peroxide tends to remain if the 100 weight sections are exceeded, it is not desirable.

[0043] Although especially the hydrogen-peroxide concentration of hydrogen peroxide solution is not limited, it is desirable that it is 3 - 30% of the weight of within the limits in respect of the solid content of generation liquid related to paint workability in the ease of dealing with it.

[0044] Moreover, aqosity liquid (A-1) can be manufactured by making hydrolysis nature titanium compound a react under existence of a titanium oxide sol for 10 minutes to 20 hours by within the limits with a hydrogen peroxide solution and a reaction temperature of 1-70 degrees C.

[0045] Aqosity liquid (A-1) by making hydrolysis nature titanium compound a react with hydrogen peroxide solution Hydrolyze with water and hydrolysis nature titanium compound a generates a hydroxyl-group content titanium compound. Subsequently, it is imagined as what is configured in the hydroxyl-group content titanium compound which the hydrogen peroxide generated, when the coordination by this hydrolysis reaction and hydrogen peroxide happens near the coincidence, it is obtained, and the chelate liquid with which stability is equal to long-term, very high preservation in a room temperature region is generated. Hydroxylation titanium gel used by the conventional process is partially three-dimensionsized by Ti-O-Ti association,

and this gel essentially differs from the object to which hydrogen peroxide solution was made to react about a presentation and stability. Moreover, a condensation reaction comes to prevent occurring and thickening in part by using a titanium oxide sol at the time of composition. The reason is considered to adsorb the front face of a titanium oxide sol and for a condensation reaction object to prevent macromolecule-ization in the solution condition.

[0046] Moreover, the titanium oxide dispersion liquid containing the ultrafine particle of the titanium oxide which crystalized the aqosity liquid (A-1) containing titanium when heat-treatment or autoclave processing was performed above 80 degrees C are obtained. At less than 80 degrees C, crystallization of titanium oxide does not fully progress. Thus, the range of 10nm or less of particle diameter of a titanium oxide ultrafine particle of the manufactured titanium oxide dispersion liquid is 1nm - 6nm preferably. Moreover, the appearance of these dispersion liquid is a translucent-like thing. Since film formation nature will fall if this particle diameter becomes larger than 10nm (a crack is produced in 1 micrometers or more), it is not desirable. These dispersion liquid can be used similarly.

[0047] The aqosity liquid (A-1) containing titanium can form the precise titanium oxide film which was excellent in adhesion with itself by heat-treating at spreading desiccation or low temperature into a steel plate ingredient.

[0048] Especially as heat-treatment temperature, it is desirable to form 200 degrees C or less of titanium oxide film at the temperature of 150 degrees C or less, for example.

[0049] The aqosity liquid (A-1) containing titanium forms the titanium oxide film of the anatase which contains a hydroxyl group a little with the above-mentioned temperature.

[0050] Since the above-mentioned aqosity liquid which used hydrolysis nature titanium compound a especially, and aqosity liquid (A-1) have the engine performance excellent in storage stability, corrosion resistance, etc. as aqosity liquid (A) of this invention, it is desirable to use this thing.

[0051] Addition distribution of other pigments and sols can also be carried out at the aqosity liquid (A) containing the above-mentioned titanium if needed. As an additive, a mica, talc, a silica, a baryta, clay, etc. can mention as an example a titanium oxide sol, titanium oxide powder, etc. which are marketed.

[0052] The compounds which are the (B) components of (Compound B) surface treatment agent are at least one sort of compounds chosen from a phosphoric-acid system compound, metal hydrofluoric acid, and a metal hydrofluoric acid salt.

[0053] As the above-mentioned phosphoric-acid system compound, condensed phosphoric acid, these salts, etc., such as mono-phosphoric acids, such as a ** phosphoric acid, a strong phosphoric acid, triphosphoric acid, the following ** phosphoric acid, hypophosphoric acid, the Tori metaphosphoric acid, a 2 ** phosphoric acid, diphosphoric acid, a PIRO ** phosphoric acid, a pyrophosphoric acid, a meta-** phosphoric acid, a metaphosphoric acid, a phosphoric acid (orthophosphoric acid), and a phosphoric-acid derivative, and these salts, the Tripoli phosphoric acid, a tetralin acid, a hexalin acid, and a condensed-phosphoric-acid derivative, are mentioned, for example, these compounds -- one sort -- or two or more sorts can be used, combining.

Moreover, as an alkali compound which forms the above-mentioned salt, organic [such as a lithium, sodium, a potassium, and ammonium] or an inorganic alkali compound is mentioned, for example. Furthermore, it is desirable to use what has solubility in water as a phosphoric-acid system compound.

[0054] Especially as a phosphoric-acid system compound, since a sodium pyrophosphate, sodium tripolyphosphate, tetralin acid sodium, a metaphosphoric acid, metaphosphoric-acid ammonium, hexametaphosphoric acid sodium, etc. demonstrate the effectiveness excellent in the storage stability of the paint, or the rust-proofing nature of a paint film, it is desirable to use this thing.

[0055] In this invention, it is thought that the compound of the aqosity liquid (A) and the phosphoric-acid system compound containing the above-mentioned titanium forms complex structure among both when the acid phosphoric-acid radical ion combined with this phosphoric-acid system compound configures to titanium ion.

[0056] moreover, the thing for which such a reaction can react easily, for example, is left in ordinary temperature (20 degrees C) by only mixing both component for about 5 minutes to

about 1 hour -- moreover -- the case where mixture is overheated compulsorily -- for example, about 30- -- it can heat for [for / about 1 minute / -] about 30 minutes at about 70 degrees C. [0057] As the above, metal hydrofluoric acid, and a metal hydrofluoric acid salt, zirconium hydrofluoric acid, titanium hydrofluoric acid, silicofluoric acid, a zirconium fluoridation salt, a titanium fluoridation salt, *****, etc. can be mentioned, for example. As what forms the salt of metal hydrofluoric acid, although sodium, a potassium, a lithium, ammonium, etc. are mentioned, a potassium and sodium are desirable and zirconium potassium fluoride, titanium potassium fluoride, sodium silicofluoride, potassium silicofluoride, etc. are mentioned as an example especially, for example.

[0058] The number of a phosphoric-acid system compound, metal hydrofluoric acid, and metal hydrofluoric acid salts is one, or two or more sorts can be mixed, they can be used, and the blending ratio of coal of a compound (B) has desirable within the limits of the 1 - 400 weight section, especially the 10 - 200 weight section to the solid content 100 weight section of the aqueous liquid (A) containing titanium.

[0059] An aqueous organic high molecular compound (C) is blended in addition to the component which the aqueous organic (high-molecular-compound C) surface treatment agent described above. If the organic resinous principle dissolved or distributed condenses an aqueous organic high molecular compound (C), and it sediments and is excellent in the stability of the aqueous liquid of the organic high molecular compound (C) itself which does not have a possibility of producing the abnormalities of thickening or gelation in water at seven or less PH, it can use a well-known thing from the former.

[0060] What has the gestalt of water solubility, water-dispersion, or emulsion nature can be used for an aqueous organic high molecular compound (C). An organic high molecular compound can be performed in water from the former as aqueous-izing, decentralization, and an approach of making it emulsion-ize using a well-known approach. As an organic high molecular compound, independently specifically Aqueous-izing and the functional group which can carry out [moisture powder]-izing for example, a hydroxyl group, a carboxyl group, an amino (imino) radical, and a sulfide radical -- The thing and need containing at least one sort, such as a phosphine radical, are accepted. A part or all of those functional groups if it is acidic resin (carboxyl group content resin etc.), ethanalamine, amine compound [such as triethylamine,], -- aqueous ammonia, if it is the thing neutralized with alkali-metal hydroxides, such as a lithium hydroxide, a sodium hydroxide, and a potassium hydroxide, and basic resin (amino-group content resin etc.) Fatty acids, such as an acetic acid and a lactic acid; what was neutralized by mineral acids, such as a phosphoric acid, can be used.

[0061] As this aqueous organic high molecular compound (C), epoxy system resin, phenol system resin, acrylic resin, urethane system resin, olefin-carboxylic-acid system resin, nylon system resin, the resin that has polyoxyalkylene chain, polyvinyl alcohol, polyglycerin, a carboxymethyl cellulose, a hydroxymethyl cellulose, hydroxyethyl cellulose, etc. are mentioned, for example. [0062] The cation system epoxy resin which comes to add an amine to an epoxy resin as the above-mentioned epoxy system resin; modified epoxy resins, such as acrylic denaturation and urethane denaturation, etc. can use it suitably. The 2nd class Monod who has an epoxy compound, an addition product (for example, refer to U.S. Pat. No. 3984299 specification), epoxy compound with the 1st class Monod or polyamine, the 2nd class Monod or polyamine, the 1 or 2nd class mixing polyamine, etc., and the ketimine-ized 1st class amino group as a cation system epoxy resin, for example, or an addition product with polyamine (for example, refer to U.S. Pat. No. 4017438 specification); the etherification resultant (for example, refer to JP.59-43013.A) of an epoxy compound and the hydroxyl compound which has the ketimine-ized 1st class amino group etc. be raised.

[0063] The above-mentioned epoxy compound has number average molecular weight within the limits of 400-4,000, especially 800-2,000, and 190-2,000, and the thing that is especially within the limits of 400-1,000 are suitable for weight per epoxy equivalent. Such an epoxy compound can be obtained by the reaction of for example, a polyphenol compound and EPIRURORUHI drine compounds. As a polyphenol compound For example, screw (4-hydroxyphenyl) -2, 2-propane, 4, and 4-dihydroxy benzophenone. A screw (4-hydroxyphenyl) -1, 1-ethane, a screw (4-

hydroxyphenyl) -1, 1-isobutane, A screw (4-hydroxy-tert-butylphenyl) -2, 2-propane, Bis(2-hydroxy naphthyl) methane, 1, 5-dihydroxy naphthalene, Bis(2, 4-dihydroxy phenyl) methane, tetrapod (4-hydroxyphenyl) -1, 1, 2, and 2-ethane, 4, and 4-dihydroxy diphenylsulfone, a phenol novolak, a cresol novolak, etc. are raised.

[0064] What heated a phenol component and formaldehyde under existence of a reaction catalyst, and made aqueous addition and the high molecular compound which is made to carry out condensation and is obtained as the above-mentioned phenol system resin can be used suitably. As the above-mentioned phenol component which is a start raw material 2 functionality phenolic compound, 3 functionality phenolic compound, the phenolic compound of four or more functionality, etc. can be used. As a 2 functionality phenolic compound o-cresol, p-cresol, p-tert-butylphenol, p-ethylphenol, 2, 3-xyleneol, 2, and 5-xyleneol etc. as a 3 functionality phenolic compound A phenol, m-cresol, m-ethylphenol, 3,5-xyleneol, m-methoxy phenol, etc. can mention bisphenol A, Bisphenol F, etc. as a 4 functionality phenolic compound. The number of these phenolic compounds is one, or two or more sorts can use them, mixing.

[0065] As the above-mentioned acrylic resin, the homopolymer with the radical of the hydrophilic property of a carboxyl group, the amino group, a hydroxyl group, etc. of a monomer or a copolymer, the copolymer of a monomer with the radical of a hydrophilic property and a monomer copolymerizable in addition to this, etc. are mentioned, for example. These are an emulsion polymerization, a suspension polymerization, or resin that carries out solution polymerization, and is denaturalized and obtained in neutralization, the aqueous-ized resin, or this resin if needed.

[0066] As the above-mentioned carboxyl group content monomer, an acrylic acid, methacrylic acid, a maleic acid, a maleic anhydride, a crotonic acid, an itaconic acid, etc. can be mentioned. [0067] As a nitrogen-containing monomer, N and N-dimethylaminoethyl (meta) acrylate and Nitrogen-containing alkyl (meta) acrylate, such as N and N-diethylaminoethyl (meta) acrylate and N-t-butylamino ethyl (meta) acrylate; Acrylamide, Methacrylamide, N-methyl (meta) acrylamide, N-ethyl (meta) acrylamide, N-methylol(meth)acrylamide, N-methoxymethyl (meta) acrylamide, N-butoxy methyl (meta) acrylamide, N, and N-dimethyl (meta) acrylamide, Polymerization nature amides;2-vinylpyridines, such as N and N-dimethylaminopropyl (meta) acrylamide, N, and N-dimethylaminoethyl (meta) acrylamide. Aromatic series nitrogen-containing monomers, such as a 1-vinyl-2-pyrrolidone and 4-vinylpyridine; allylamine etc. is mentioned.

[0068] As a hydroxyl-group content monomer, the compound which carried out ring opening polymerization of the epsilon-caprolactone to the monoester ghost with polyhydric alcohol and acrylic acids, such as 2-hydroxyethyl (meta) acrylate, hydroxypropyl (meta) acrylate, 2, 3-dihydroxy butyl (meta) acrylate, 4-hydroxy butyl (meta) acrylate, and polyethylene-glycol monochrome (meta) acrylate, the monoester ghost; above-mentioned polyhydric alcohol with a methacrylic acid and an acrylic acid, or a methacrylic acid is mentioned.

[0069] As a monomer, in addition, methyl (meta) acrylate, ethyl (meta) acrylate, n-propyl (meta) acrylate, isopropyl (meta) acrylate, n-butyl (meta) acrylate, isobutyl (meta) acrylate, tert-butyl (meta) acrylate, 2-ethylhexyl acrylate, n-octyl (meta) acrylate, lauryl (meta) acrylate, Alkyl (meta) acrylate of the carbon numbers 1-24, such as tridecyl (meta) acrylate, octadecyl (meta) acrylate, and isostearyl (meta) acrylate; styrene, vinyl acetate, etc. are mentioned. The number of these compounds is one, or they can be used combining two or more sorts. In this invention, "acrylate (meta)" means acrylate or methacrylate.

[0070] As the above-mentioned urethane system resin, the need is accepted in the polyurethane which consists of polyol and diisocyanate, such as polyester polyol and polyether polyol. Diol. Chain expanding is carried out under existence of the chain expanding agent which is a low molecular weight compound with two or more active hydrogen, such as diamine, what was distributed or dissolved in stability can be used suitably, and a well-known thing can be used underwater widely (for example, JP.42-24192.B --) Refer to JP.42-24194.B, JP.42-5118.B, JP.49-986.B, JP.49-33104.B, JP.50-15027.B, and JP.53-29175.B. As an approach of distributing or dissolving polyurethane resin underwater in stability, the following approach can be used, for example.

[0071] (1) How to give a hydrophilic property, and distribute or dissolve underwater by self-

emulsification by introducing ionicity radicals, such as a hydroxyl group, an amino group, and a carboxyl group, into the side chain or end of a polyurethane polymer.

[0072] (2) How to distribute compulsorily underwater the polyurethane polymer which blocked the polyurethane polymer or end isocyanate radical which the reaction completed by block agents, such as an oxime, alcohol, a phenol, a mercaptan, an amine, and sodium bisulfite, using an emulsifier and mechanical shearing force. How to mix with water / emulsifier / chain expanding agent the urethane polymer which furthermore has an end isocyanate radical, and to perform decentralization and macromolecule quantification to coincidence using mechanical shearing force.

[0073] (3) How to use the water-soluble polyol like a polyethylene glycol as polyol of a polyurethane main raw material, and distribute or dissolve in water underwater as meltable polyurethane.

[0074] About the above-mentioned distribution or the dissolution approach, it is not limited to the single approach by the above-mentioned polyurethane system resin, and the mixture obtained by each approach can also be used for it.

[0075] As diisocyanate which can be used for composition of the above-mentioned polyurethane system resin. The diisocyanate of aromatic series, an alicyclic group, and aliphatic series is mentioned. Specifically Hexamethylene di-isocyanate, Tetramethylene di-isocyanate, 3, 3'-dimethoxy -4, 4'-biphenylene di-isocyanate, p-xylylene diisocyanate, m-xylylene diisocyanate, 1, 3-(G SOSHIANATO methyl) cyclohexanone, 1, 4-(G SOSHIANATO methyl) cyclohexanone, 4, a 4'-G SOSHIANATO cyclohexanone, 4, 4'-methylenebis (cyclohexyl isocyanate), Isophorone diisocyanate, 2, 4-tolylene diisocyanate, 2, 6-tolylene diisocyanate, p-phenylene diisocyanate, Diphenylmethane diisocyanate, m-phenylene diisocyanate, 2, 4-naphthalene diisocyanate, 3, the 3'-dimethyl -4, 4'-biphenylene di-isocyanate, 4, 4'-biphenylene di-isocyanate, etc. are mentioned. 2, 4-tolylene diisocyanate, 2, 6-tolylene diisocyanate, hexamethylene di-isocyanate, and especially isophorone diisocyanate are [among these] desirable.

[0076] as the commercial item of the above-mentioned polyurethane system resin -- hide run HW-330 -- said -- HW-340 -- said -- HW-350 (all are the Dai-ichi Ink & Chemicals, Inc. make) and super FREX 100 -- said -- 150, this F-3438D (all are the Dai-ichi Kogyo Seiyaku Co., Ltd. make), etc. can be mentioned.

[0077] As the above-mentioned polyvinyl alcohol resin, it is desirable that it is 87% or more of polyvinyl alcohol whenever [saponification], and it is desirable that it is 98% or more of the so-called full saponification polyvinyl alcohol whenever [saponification] especially, and it is suitable that number average molecular weight is within the limits of 3,000-100,000.

[0078] The blocking polyoxy alkylene glycol which what has a polyoxyethylene chain or a polyoxypropylene chain could use suitably as resin which has the above-mentioned polyoxyalkylene chain, for example, the polyethylene glycol, the polypropylene glycol, the above-mentioned polyoxyethylene chain, and the above-mentioned polyoxypropylene chain combined in the shape of a block can be mentioned.

[0079] As the above-mentioned olefin-carboxylic-acid system resin, water-dispersion [at least one sort of] or water soluble resin chosen from two sorts, copolymer [of olefins, such as ethylene and a propylene, and polymerization nature unsaturated carboxylic acid] ** and resin ** which adds and carries out the emulsion polymerization of the polymerization nature unsaturated compound to the dispersion liquid of this copolymer, and comes to construct a bridge in a particle further, can be used.

[0080] The above-mentioned copolymer **s are one sort of an olefin and unsaturated carboxylic acid, such as an acrylic acid (meta) and a maleic acid, or two sorts or more of copolymers. In this copolymer **, it is suitable that the content of this unsaturated carboxylic acid is 5 - 40% of the weight of within the limits preferably three to 60% of the weight, and the acid radical in a copolymer can be distributed in water by neutralizing by the alkali.

[0081] The above-mentioned resin ** is bridge formation resin which adds and carries out the emulsion polymerization of the polymerization nature unsaturated compound to the water dispersion of copolymer **, and comes to construct a bridge in a particle further. As this polymerization nature unsaturated compound, the vinyl monomers enumerated, for example by

explanation of said water-dispersion or water-soluble acrylic resin are mentioned, and one sort or two sorts or more can be used, choosing them suitably.

[0082] The blending ratio of coal of an aqosity organic high molecular compound (C) has desirable within the limits of the 10 - 2,000 weight section, especially the 100 - 1,000 weight section from points, such as the stability of liquid, and anti-corrosiveness, to the solid content 100 weight section of the aqosity liquid (A) containing titanium.

[0083] Since a surface treatment agent serves as a stable liquid in neutrality or an acid field, especially its PHs 1-7, especially range of 1-5 are desirable.

[0084] In a surface treatment agent, pigments, such as a thickener, a surface active agent, an antimicrobial agent, rust-proofers (a tannic acid, phytic acid, benzotriazol, etc.), a color pigment, an extender, and a rust preventive pigment, can be contained if needed in addition to the above-mentioned component.

[0085] Moreover, it can be diluted and used for a surface treatment agent if needed with hydrophilic solvents, such as a methanol, ethanol, isopropyl alcohol, an ethylene glycol system, and a propylene glycol system.

[0086] Next, the paint steel plate of this invention is explained to a detail.

[0087] Especially as a substrate metallic material used for the paint steel plate of paint steel plate this invention, it is not restricted and cold rolled sheet steel, a hot-dip zinc-coated carbon steel sheet, an electrolytic zinc-coated carbon steel sheet, an iron-zinc alloy plating steel plate, a nickel-zinc alloy plating steel plate, an aluminum-zinc alloy plating steel plate (for example, alloy-plating steel plate currently sold by the trade name of "gal barium" and "Galle Hwang"), an aluminum plating steel plate, an aluminum plate, etc. can be mentioned. Moreover, although the non-processed thing is usually suitable as a substrate metallic material, even if it uses it for what performed chemical conversion, such as chromate treatment, phosphoric-acid zinc processing, and compound oxide-film processing, there is especially no problem.

[0088] The front face of the above-mentioned substrate metallic material is made to apply and dry said surface treatment agent, and a surface treatment coat is formed.

[0089] A surface treatment agent can be painted on a substrate metallic material (assembled) by the method of application of itself known, for example, dip coating, shower paint, spray painting, roll coating, electropainting, etc. it is suitable for the desiccation conditions of a surface treatment agent to make it usually dry for about 2 seconds to about 30 minutes on the conditions from which a material attainment maximum temperature becomes about 60-250 degrees C.

[0090] Moreover, especially as desiccation coat thickness of a surface treatment agent, the range of 0.1-3 micrometers is usually desirable 0.001-10 micrometers. If engine performance, such as corrosion resistance and a water resisting property, is inferior when set to less than 0.001 micrometers, and it exceeds 10 micrometers on the other hand, since the surface treatment film will break or workability will fall, it is not desirable.

[0091] A finishing paint film is covered without minding through an under coat paint film on the above-mentioned surface treatment coat. What is necessary is for there to be especially no limit by the class of the primer and top coat, and just to select it suitably according to the purpose. For example, a coating constituent is baked on the solvent mold coating from the gestalt, a water genotype coating, a fine-particles mold coating, etc. from the hardening method, and from the appearance of the paint film obtained by applying a coating constituent and drying, although it can classify into a coloring coating, a metallic paint, a clear coating, etc., it can use all for a hardening mold coating, a photo-curing mold coating, an air drying coating, etc. again.

[0092] Although a finishing paint film may be an one quart 1BEKU mold, it can use known approaches, such as two quart 1 BEKU, two quart 2 BEKU, and three quart 1 BEKU, and may form a finishing paint film through a middle-coat paint film on an under coat paint film.

[0093] Furthermore, organic coating which has functionality, such as lubricity and fingerprint-proof nature, in addition to the top coat aiming at the usual beautiful decoration can also be applied as finishing.

[0094] What is necessary is to be able to use the object for building materials, the object for household electric appliances, the object for automobiles, the object for cans, etc. for the

application of a paint steel plate that there is especially no limit in the application which is using the paint steel plate conventionally, and just to select paint of the primer and top coat suitably with the configuration of the application and a coated object etc. For example, when a spray, a brush, electrodeposition, etc. are suitable in painting to what was fabricated, and painting to tabular things, such as a precoat paint steel plate, roll coating, curtain flow coating, etc. are used suitably.

[0095]

[Effect of the Invention] It is thought that this invention produces the following effectiveness from having the above-mentioned configuration.

[0096] The surface treatment agent which has the above-mentioned configuration in this invention for example, by painting and heating to metal bases, such as a steel plate, and forming a surface treatment coat. The phosphoric-acid system compound which is the (B) component which constitutes a surface treatment agent, metal hydrofluoric acid, a metal hydrofluoric acid salt, etc. act as a metal etching agent, and, on the other hand, with the aqosity liquid (A) and the aqosity organic high molecular compound (C) containing titanium it excels in adhesion with a material, that in which an oxygen penetrable and steam penetrable small coat is formed is conjectured, and a paint steel plate with very high anti-corrosiveness and endurance is obtained.

[0097]

[Example] Hereafter, an example and the example of a comparison are given and this invention is explained still more concretely. Hereafter, the "weight section" and "% of the weight" are meant the "section" and "%", respectively. This invention is not restricted to the following examples. [0098] Aqueous ammonia (1:9) was dropped at the solution which set five cc of 60% solutions of example of manufacture manufacture 1 titanium tetrachlorides of titanium system aqosity liquid to 500 cc with distilled water, and hydroxylation titanium was settled. With distilled water, ten cc of 30% solutions of hydrogen peroxide solution was added, they were stirred after washing, and titanium system aqosity liquid (A1) of 2% of solid content with the viscosity containing titanium of yellow translucence was obtained.

[0099] It was dropped agitating at 20 degrees C in the mixture of the 30% hydrogen-peroxide-solution 10 section and the deionized water 100 section having covered [of the example of manufacture 2 tetrapod iso-propoxytitanium 10 section, and the iso-propanol 10 section] it for 1 hour. It riped at 25 degrees C after that for 2 hours, and titanium system aqosity liquid (A2) of 2% of solid content of yellow transparency which is viscous for a while was obtained.

[0100] Titanium system aqosity liquid (A3) of 2% of solid content was obtained on the same manufacture conditions using tetra-n-butoxytitanium instead of the tetra-iso-propoxytitanium of the example of manufacture of example of manufacture 3 titanium system aqosity liquid (A2).

[0101] Titanium system aqosity liquid (A4) of 2% of solid content was obtained on the same manufacture conditions using the trimer of tetra-iso-propoxytitanium instead of the tetra-iso-propoxytitanium of the example of manufacture of example of manufacture 4 titanium system aqosity liquid (A2).

[0102] In the example of manufacture of example of manufacture 5 titanium system aqosity liquid (A2), hydrogen peroxide solution was dropped over 1 hour at 50 degree C of ***** 3 times, it riped at 60 more degrees C for 3 hours, and titanium system aqosity liquid (A5) of 2% of solid content was obtained.

[0103] The example of manufacture 6 titanium system water solution (A3) was heat-treated at 95 degrees C for 6 hours, and titanium system aqosity liquid (A6) of 2% of solid content with translucent white yellow was obtained.

[0104] The mixture of the example of manufacture 7 tetrapod iso-propoxytitanium 10 section and the iso-propanol 10 section was dropped agitating at 10 degrees C in the mixture of the five sections (solid content), the 30% hydrogen-peroxide-solution 10 section, and the deionized water 100 section having TKS-applied it for 1 hour (the TAYCA CORP. make, titanium oxide sol). It riped at 10 degrees C after that for 24 hours, and titanium system aqosity liquid (A7) of 2% of solid content of yellow transparency which is viscous for a while was obtained.

[0105] In the 4 Thu openings flask of 1L equipped with example of manufacture manufacture 8

thermometer of acrylic resin, ***** the condensor, and the dropping funnel Put in the isopropyl alcohol 180 section and the temperature after a nitrogen purge and in a flask is adjusted to 85 degrees C. The ethyl acrylate 140 section, the methyl methacrylate 68 section, the styrene 15 section, About 2 hours is required and dropped with the catalyst which consists of the 2 and 2'-azobis (2, 4-dimethyl WAREO nitril) 8 section the monomer mixture which consists of the N-n-butoxy methylacrylamide 15 section, the 2-hydroxyethyl acrylate 38 section, and the acrylic-acid 24 section. It is the after [dropping termination] said temperature, and if a reaction is continued for further 5 hours, about 63% of solid content and the transparent and colorless resin solution of the acid number 67 [about] will be obtained for conversion about 100%. The dimethylamino ethanol 108 section was mixed to this resin solution 500 section, and the acrylic resin water dispersion (C1) of 30% of solid content was obtained by fully stirring after adding water.

[0106] After adding Epicoat 1009 resin (epoxy resin by shell chemistry company, molecular weight 3,750) 1,880g (0.5 mols), and 1,000g of mixed solvents of methyl isobutyl ketone / xylene = 1 / 1 (weight ratio) to the reactor equipped with the example of manufacture manufacture 9 stirring equipment of an amine modified epoxy resin, a reflux condenser, a thermometer, and liquid dropping equipment, stirring heating was carried out and it dissolved in it at homogeneity. It cooled to 70 degrees C after that, and for 30 minutes was required and JI (n-propanol) amine 70g isolated preparatively to liquid dropping equipment was dropped. In the meantime, reaction temperature was held at 70 degrees C. The amine modified epoxy resin of 68% of solid content was obtained by holding at 120 degrees C after dropping termination for 2 hours, and completing a reaction. The amine modified epoxy resin water dispersion (C2) of 30% of solid content was obtained by mixing 88% of formic acid 25 section to 1,000g of obtained resin, and fully stirring after adding water.

[0107] The manufacture surface treatment agent S1 (for examples) of a surface treatment agent The 2% titanium system aqosity liquid (A1) 50 section, the 20% zirconium hydrofluoric acid 5 section, the 30% acrylic resin water dispersion (C1) 10 section, and the deionized water 35 section were blended, and the surface treatment agent S1 was obtained.

[0108] Each surface treatment agent was obtained like the example of manufacture of the above-mentioned surface treatment agent S1 except the combination shown in surface treatment agent S2-S11 (for examples) and surface treatment agent H1 - H3 (for the examples of a comparison) table 1.

[0109]

[Table 1]

表1(下地処理剤の組成例)

下地処理剤例	実 施 例											比較例		
	S1	S2	S3	S4	S5	S6	S7	S8	S9	S10	S11	H1	H2	H3
25%アクリル系樹脂(A1)	50	50	50	50	50	50								
20%ジメチルアミン(A2)							50							50
25%ジメチルアミン(A3)								50						50
25%ジメチルアミン(A4)									50					50
25%ジメチルアミン(A5)										50				50
25%ジメチルアミン(A6)											50			50
25%ジメチルアミン(A7)												50		50
20%ジメチルアミン(A8)													50	50
20%ジメチルアミン(A9)														50
20%ジメチルアミン(A10)														50
20%ジメチルアミン(A11)														50
20%ジメチルアミン(A12)														50
20%ジメチルアミン(A13)														50
20%ジメチルアミン(A14)														50
20%ジメチルアミン(A15)														50
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20%ジメチルアミン(A99)														50
20%ジメチルアミン(A100)														50

(※) 例1: 20%ジメチルアミン(A1) + 20%ジメチルアミン(A2) + 20%ジメチルアミン(A3) + 20%ジメチルアミン(A4) + 20%ジメチルアミン(A5) + 20%ジメチルアミン(A6) + 20%ジメチルアミン(A7) + 20%ジメチルアミン(A8) + 20%ジメチルアミン(A9) + 20%ジメチルアミン(A10) + 20%ジメチルアミン(A11) + 20%ジメチルアミン(A12) + 20%ジメチルアミン(A13) + 20%ジメチルアミン(A14) + 20%ジメチルアミン(A15) + 20%ジメチルアミン(A16) + 20%ジメチルアミン(A17) + 20%ジメチルアミン(A18) + 20%ジメチルアミン(A19) + 20%ジメチルアミン(A20) + 20%ジメチルアミン(A21) + 20%ジメチルアミン(A22) + 20%ジメチルアミン(A23) + 20%ジメチルアミン(A24) + 20%ジメチルアミン(A25) + 20%ジメチルアミン(A26) + 20%ジメチルアミン(A27) + 20%ジメチルアミン(A28) + 20%ジメチルアミン(A29) + 20%ジメチルアミン(A30) + 20%ジメチルアミン(A31) + 20%ジメチルアミン(A32) + 20%ジメチルアミン(A33) + 20%ジメチルアミン(A34) + 20%ジメチルアミン(A35) + 20%ジメチルアミン(A36) + 20%ジメチルアミン(A37) + 20%ジメチルアミン(A38) + 20%ジメチルアミン(A39) + 20%ジメチルアミン(A40) + 20%ジメチルアミン(A41) + 20%ジメチルアミン(A42) + 20%ジメチルアミン(A43) + 20%ジメチルアミン(A44) + 20%ジメチルアミン(A45) + 20%ジメチルアミン(A46) + 20%ジメチルアミン(A47) + 20%ジメチルアミン(A48) + 20%ジメチルアミン(A49) + 20%ジメチルアミン(A50) + 20%ジメチルアミン(A51) + 20%ジメチルアミン(A52) + 20%ジメチルアミン(A53) + 20%ジメチルアミン(A54) + 20%ジメチルアミン(A55) + 20%ジメチルアミン(A56) + 20%ジメチルアミン(A57) + 20%ジメチルアミン(A58) + 20%ジメチルアミン(A59) + 20%ジメチルアミン(A60) + 20%ジメチルアミン(A61) + 20%ジメチルアミン(A62) + 20%ジメチルアミン(A63) + 20%ジメチルアミン(A64) + 20%ジメチルアミン(A65) + 20%ジメチルアミン(A66) + 20%ジメチルアミン(A67) + 20%ジメチルアミン(A68) + 20%ジメチルアミン(A69) + 20%ジメチルアミン(A70) + 20%ジメチルアミン(A71) + 20%ジメチルアミン(A72) + 20%ジメチルアミン(A73) + 20%ジメチルアミン(A74) + 20%ジメチルアミン(A75) + 20%ジメチルアミン(A76) + 20%ジメチルアミン(A77) + 20%ジメチルアミン(A78) + 20%ジメチルアミン(A79) + 20%ジメチルアミン(A80) + 20%ジメチルアミン(A81) + 20%ジメチルアミン(A82) + 20%ジメチルアミン(A83) + 20%ジメチルアミン(A84) + 20%ジメチルアミン(A85) + 20%ジメチルアミン(A86) + 20%ジメチルアミン(A87) + 20%ジメ

side in the above-mentioned table 1 on it after cleaning washing were painted so that desiccation thickness might be set to 0.3 micrometers, and it could be burned on the conditions from which PMT (the highest attainment temperature of a steel plate) becomes 100 degrees C in 15 seconds, and each test color card was created. Subsequently, on each obtained processing plate, KOSUMA 2050 (the Kansai Paint Co., Ltd. make, a trade name, an acrylic / silica compound-ized resin liquid) was painted so that desiccation thickness might be set to 3 micrometers, and it could be burned on the conditions which become PMT120 degree C in 20 seconds, and each test panel was created.

[0111] Corrosion resistance and adhesion of the upper paint film were examined to each obtained test color card. The test result is shown in the after-mentioned table 2. The trial was performed according to the following test method.

[0112] Corrosion resistance. To the test color card which carried out the seal of the edge surface part and flesh-side surface part of a test color card, it is JIS. The salt spray test specified to Z2371 was performed till 240 hours, and the following criteria estimated extent of the rust of the paint film side at the time of 120-hour progress and 240-hour progress.

a: b in which generating of white rust is not accepted : for generating extent of less than 10% and d:white rust, generating extent of less than 50% and e:white rust is [generating extent of white rust / generating extent of less than 5% of paint film area, and c:white rust / area / 5% or more of / paint film] 50% or more of paint film area in 10% or more of paint film area.

[0113] Adhesion of the upper paint film: It painted so that desiccation thickness might become a test color card with 30 micrometers about Amylac #1000 White (the Kansai Paint Co., Ltd. make, heat-curing mold alkyd resin coating, white), and it could be burned for 20 minutes at 130 degrees C, and the top coat plate -1 was obtained. Moreover, independently, it painted so that desiccation thickness might become a test color card with 30 micrometers about serious kuron #1000 White (the Kansai Paint Co., Ltd. make, heat-curing mold acrylic resin coating, white), and it could be burned for 20 minutes at 150 degrees C, and the top coat plate -2 was obtained.

About the top coat plate -1 and the top coat plate -2 which were obtained, the blemish of 11 every direction each which reaches a base with a knife was put into the paint film side in a grid pattern, and 100 grids of 1mm angle were created. The following criteria estimated exfoliation extent of the upper paint film at the time of sticking cellophane adhesive tape in this squares section, and removing a tape in an instant.

a: d in which 3-10 exfoliations of the copper paint film 1-2 exfoliations of the bupper paint film are accepted to be exfoliations of the upper paint film are not accepted to be at all are accepted : ten or more exfoliations of the upper paint film are accepted.

[0114]

[Table 2]

		検査方法(1)			上層塗膜の密着性
		下地塗膜剥離	密着性	120時間	
No					
実施例 1	S1	a	b	a	a
実施例 2	S2	a	b	a	a
実施例 3	S3	a	a	a	a
実施例 4	S4	a	a	a	a
実施例 5	S5	a	b	a	a
実施例 6	S6	a	a	a	a
実施例 7	S7	a	b	a	a
実施例 8	S8	a	a	a	a
実施例 9	S9	a	b	a	a
実施例 10	S10	a	b	a	a
実施例 11	S11	a	a	a	a
比較例 1	H1	b	c	c	c
比較例 2	H2	b	d	c	c
比較例 3	H3	b	c	c	c

[0115] After cleaning washing and on it, the hot-dip zinc-coated carbon steel sheet of plating coating weight 120 g/m² of 0.4mm of the method-of-application (2) examples 12-22 and the

example 4 of a comparison - 6 board thickness and one side was painted so that desiccation thickness might be set to 0.3 micrometers in the above-mentioned surface treatment agent, and the processing plate was created on the conditions from which PMT (the highest attainment temperature of a steel plate) becomes 100 degrees C in 10 seconds, subsequently, this processing plate top -- KP color 8000 primer (the Kansai Paint Co., Ltd. make --) Paint a denaturation epoxy system coating so that desiccation thickness may be set to 5 micrometers, and a paint film is formed on the conditions from which PMT becomes 210 degrees C in 20 seconds. Subsequently, each test color card which paints KP color 1580 White (the Kansai Paint Co., Ltd. make, a polyester resin system coating, white) so that desiccation thickness may be set to 15 micrometers, bakes on this primer coat on the conditions from which PMT becomes 215 degrees C in 40 seconds, and has the upper paint film was created. About these test color cards, the adhesion of the upper paint film and a corrosion resistance and damp-proof trial were performed. The test result is shown in the after-mentioned table 3. Each trial was performed according to the following test method.

[0116] Adhesion of the upper coating: The blemish of 11 every direction each which reaches a base with a knife was put into the paint film side in a grid pattern, and 100 grids of 1mm angle were created. The following criteria estimated exfoliation extent of the upper paint film at the time of sticking cellophane adhesive tape in this squares section, and removing a tape in an instant.

a: d in which 3-10 exfoliations of the copper paint film 1-2 exfoliations of the bupper paint film are accepted to be exfoliations of the upper paint film are not accepted to be at all are accepted : ten or more exfoliations of the upper paint film are accepted.

[0117] Corrosion resistance: After carrying out the seal of the edge surface part and the flesh-side surface part of a test color card which were cut in magnitude of 70x150mm and which have the upper paint film, the salt spray test specified to JISZ2371 about the paint plate which prepared 4T bending section (part which carried out the paint film side outside, bent 180 degrees on both sides of four spacers of 0.4mm thickness, and was processed) in the upper part of a test color card, and prepared the cross-cut section in the lower part of a test color card was performed for 1000 hours. The following criteria estimated generating extent of the white rust in 4T bending section in the paint plate after a trial, the blister width of face of the cross-cut section, and blister generating extent of the general section (center section without processing and a cut).

[Blister generating extent of the general section]

a: b: in which generating of a blister is not accepted -- c: in which generating of a blister is accepted slightly -- d: in which generating of a remarkable blister is accepted -- generating of a remarkable blister is accepted.

[Blister width of face of the cross-cut section]

a: For less than 2mm and the single-sided blister width of face from c:cross cut, less than 5mm and the single-sided blister width of face from dcross cut are [the single-sided blister width of face from a cross cut / less than 1mm and the single-sided blister width of face from b:cross cut] 5mm or more at 2mm or more in 1mm or more.

[4T Generating extent of the white rust in the bending section]

a: b in which generating of white rust is not accepted : slightly, generating and d:white rust are quite remarkable and generating and c:white rust are generated by white rust.

[0118] Moisture resistance: About the test color card which carried out the seal of the edge surface part and flesh-side surface part of a test color card which have the upper paint film, it is JIS, K5400 The humidity resistance test was performed according to 9.2.2. Test time could be 1000 hours on the conditions whose relative humidity the temperature in a humidity resistance test machine box is 49 degrees C, and is 95 - 100%. The following criteria estimated blister generating extent of the paint film of the test color card after a trial.

a: b: in which generating of a blister is not accepted -- c: in which generating of a blister is accepted slightly -- d: in which generating of a remarkable blister is accepted -- generating of a remarkable blister is accepted.

[Table 3]

表3

下地処理剤 No	上層塗料 の密着性	塗装方法(2)		耐湿性
		一般部	耐食性 加工外側部	
実施例12	S1	a	b	a
実施例13	S2	a	b	a
実施例14	S3	a	a	a
実施例15	S4	a	a	a
実施例16	S5	a	a	a
実施例17	S6	a	a	a
実施例18	S7	a	a	a
実施例19	S8	a	a	a
実施例20	S9	a	a	a
実施例21	S10	a	a	a
実施例22	S11	a	a	a
比較例4	H1	c	c	b
比較例5	H2	c	c	b
比較例6	H3	c	c	b

[0120] 0.6mm of the method-of-application (3) examples 23-33 and the example 7 of a comparison - 9 board thickness. The electrolytic zinc-coated carbon steel sheet of plating coating weight 20 g/m² of one side After cleaning washing. The surface treatment agent shown in the above-mentioned table 1 on it is painted so that desiccation thickness may be set to 0.3 micrometers. After being burned on the conditions from which PMT (the highest attainment temperature of a steel plate) becomes 100 degrees C in 15 seconds, Serious kuron #1000 White (the Kansai Paint Co., Ltd. make, heat-curing mold acrylic resin coating, white) was painted so that desiccation thickness might be set to 30 micrometers, and it could be burned for 20 minutes at 150 degrees C, and each test color card was created.

[0121] About each obtained test color card, corrosion resistance and adhesion of a paint film were examined. The test result is shown in the after-mentioned table 4. The trial was performed according to the following test method.

[0122] Adhesion of a paint film: The blemish of 11 every direction each which reaches a base with a knife was put into the paint film side in a grid pattern, and 100 grids of 1mm angle were created. The following criteria estimated exfoliation extent of the upper paint film at the time of sticking cellophane adhesive tape in this squares section, and removing a tape in an instant.
a: d in which 3-10 exfoliations of the upper paint film 1-2 exfoliations of the bupper paint film are accepted to be exfoliations of the upper paint film are not accepted to be at all are accepted : ten or more exfoliations of the upper paint film are accepted.

[0123] Corrosion resistance: To the test color card which carried out the seal of the edge surface part and flesh-side surface part of a test color card, it is JIS. While the salt spray test specified to Z2371 was performed till 240 hours and the following criteria estimated extent of the rust of the general paint film section, and extent of blistering of the cross-cut section, the paint film exfoliation width (mm) after removing the cross-cut section on a tape was indicated.

[White rust generating extent of the general section]

a: b in which generating of white rust is not accepted : for generating extent of less than 10% and d:white rust, generating extent of less than 50% and e:white rust is [generating extent of white rust / generating extent of less than 5% of paint film area, and c:white rust / area / 5% or more of / paint film] 50% or more of paint film area in 10% or more of paint film area.

[Blister width of face of the cross-cut section]

a: For less than 2mm and the single-sided blister width of face from c:cross cut, less than 5mm and the single-sided blister width of face from d:cross cut are [the single-sided blister width of face from a cross cut / less than 1mm and the single-sided blister width of face from b:cross cut] 5mm or more at 2mm or more in 1mm or more.

[0124]

[Table 4]

表4

下地処理剤 No	海塩の 密着性	塗装方法(3)		耐食性 加工外側部	加工外側部ノーマル 2.0mm
		一般部	耐食性 加工外側部		
実施例23	S1	a	b	a	2.0
実施例24	S2	a	b	a	2.0
実施例25	S3	a	a	a	1.0
実施例26	S4	a	a	a	1.5
実施例27	S5	a	a	a	2.5
実施例28	S6	a	a	a	1.0
実施例29	S7	a	a	a	2.0
実施例30	S8	a	a	a	2.0
実施例31	S9	a	a	a	2.5
実施例32	S10	a	a	a	2.5
実施例33	S11	a	a	a	1.0
比較例7	H1	c	a	a	10.0
比較例8	H2	c	a	a	7.0
比較例9	H3	c	a	a	5.0

[0125] To #5182 aluminum plate with the method-of-application (4) examples 34-44 and an example [of a comparison / 10] - a 12 thickness of 0.27mm, after cleaning washing. The surface treatment agent shown in the above-mentioned table 1 on it is painted so that desiccation thickness may be set to 0.3 micrometers. Epicoat 1009 (Japan epoxy resin company make ---) after being burned on the conditions which serve as PMT 100 degree C in 15 seconds The bisphenol A mold epoxy resin, weight-per-epoxy-equivalent 3,500, and number-average-molecular-weight 3,750 80 section. The clear coating which consists of the HITANORU 4020 (Hitachi Chemical Co., Ltd. make, phenol resin) 20 section and the phosphoric-acid 0.4 section was painted by the roll coater so that dry paint film weight might serve as 120 mg/cm², the inside of the hot-air-drying furnace of a conveyor conveyance type was passed, it baked, and the test color card was obtained. 240 degrees C and drying-furnace secret communication fault time amount made [PMT] printing conditions the conditions for 20 seconds. Based on the following test method, various trials were performed about the obtained test color card. The test result is shown in the after-mentioned table 5.

[0126] Test-method workability : Using a special goby chip box mold E. I. du Pont de Nemours impact test machine, the one lower part is installed in a tester on both sides of an aluminum plate with a thickness of 0.3mm between the bending sections of the test color card used as 2 chip boxes so that a paint film side may become outside. After the contact surface's having dropped the spindle of iron with an even thickness of 1kg from height of 50cm, having bent and giving an impact to the section, the current value (mA) of 2mm width of face of 6.5 bending points at the time of passing the electrical potential difference of V for 6 seconds was measured to the bending point, and the following criteria estimated.

O : for less than 1.0mA and **current value, less than 5.0mA and x:current value are [a current value / less than 0.5mA and O:current value] 5.0mA or more at 1.0mA or more in 0.5mA or more.

[0127] Processing section corrosion resistance : the can top which performed **** processing of a test color card using the **** press machine It winds and fastens to the boiler barrel filled up with the water solution which dissolved the malic-acid 2 section, the citric-acid 2 section, and the salt 2 section in the deionized water 100 section. After the paint film side of this test color card by which **** processing was carried out stored for five days in the condition of having been immersed in contents in the 50-degree C interior of a room, the can was cleared, the condition of a can top was observed and the following criteria estimated.

O : although rust is not accepted in O:can top abnormalities are not accepted to be to a can top, rust is remarkably accepted in x:can top rust is accepted to be to **can top ***** or change is accepted to be for a while.

[0128] Film [---proof] remainder nature (feather [---proof] ring nature): **** processing was performed to the test color card like the case where processing section corrosion resistance is evaluated, opening was carried out so that opening of that lid might be pulled up in the

condition of having turned this can top ebullition underwater [100-degree C], and having turned the paint film side down after immersion for 10 minutes, and the following criteria estimated the exfoliation width of face of the paint film from an open end.

O : for less than 0.5mm and the maximum exfoliation width of face of **paint film, less than 1.0mm and the maximum exfoliation width of face of x:paint film are [the maximum exfoliation width of face of a paint film / less than 0.2mm and the maximum exfoliation width of face of O:paint film] 1.0mm or more at 0.5mm or more in 0.2mm or more.

[0129] Retort [-proof] milkiness nature: The following criteria estimated the milkiness condition of a paint film of it having been immersed in water and having processed the test color card for 30 minutes at 125 degrees C in the autoclave.

O : -- O: in which milkiness is not accepted at all -- **: in which milkiness is accepted very slightly -- x: in which milkiness is accepted for a while --- milkiness is accepted remarkably.

[0130] Health nature: It put into the bottle made from heat-resisting glass, and it covered, processing was performed for 30 minutes at 125 degrees C in the autoclave, and health nature was evaluated by the rate that the amount of the tap water which carried out activated carbon treatment of the tap water which carried out activated carbon treatment to the test color card to 2 the painting area of 1cm of a test color card is set to one cc, based on the consumption (ppm) of potassium permanganate according to the method of examining the Food Sanitation Law publication about the contents liquid after processing.

O : for 1 ppm or more less than 3 ppm and **:consumption, 3 ppm or more less than 10 ppm and x:consumption are [consumption / less than 1 ppm and O:consumption] 10 ppm or more.

[0131] Adhesive property: What the nylon film was put [what], this was heated [what] for 60 seconds at 200 degrees C, and it pressurized [what] for 30 seconds at 200 degrees C after that, and carried out welding of the nylon to both paint films by making the paint film side of the test color card (150x5mm) of two sheets into a covering side was used as the test piece. Next, T mold peel strength of this test piece was measured using the tension tester (Shimazu autograph AGS-500A) on with a 200mm temperature [in tension rate / a part for /and temperature of 20 degrees C] conditions. The following criteria estimated 5 times of the averages.

O : it is 3kg / less than 5mm, and **:1kg / 5mm or more in 3kg / 5mm or more, and O:2kg / 5mm or more, and they are 2kg / less than 5mm, and x:1kg / less than 5mm.

[0132]

[Table 5]

表5

試験項目	No	試験方法 (4)			
		加工性	加工時耐食性	耐食性	衛生性
実験例34	S1	○	○	○	○
実験例35	S2	○	○	○	○
実験例36	S3	○	○	○	○
実験例37	S4	○	○	○	○
実験例38	S5	○	○	○	○
実験例39	S6	○	○	○	○
実験例40	S7	○	○	○	○
実験例41	S8	○	○	○	○
実験例42	S9	○	○	○	○
実験例43	S10	○	○	○	○
実験例44	S11	○	○	○	○
比較例10	H1	○	○	○	○
比較例11	H2	△	△	△	×
比較例12	H3	○	△	○	△

[Translation done.]